

## PATENT ABSTRACTS OF JAPAN

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(30)Priority

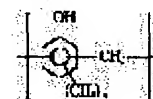
Priority number : 06164634 Priority date : 23.06.1994 Priority country : JP

## (54) POSITIVE RESIST COMPOSITION FOR LIFT-OFF METHOD AND PATTERN FORMING METHOD

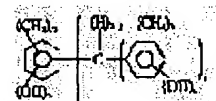
(57)Abstract:

PURPOSE: To provide a resist compsn. capable of forming a resist pattern ensuring high working precision and high reliability by a lift-off method and to provide a pattern forming method.

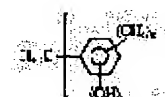
CONSTITUTION: A positive resist compsn. contg. novolak resin having repeating units represented by formula I as an alkali-soluble resin, a low nuclear body represented by formula II or III and having phenolic hydroxyl groups and 2-5 benzene rings as a dissolution inhibitor and a compd. having a 1,2-naphthoquinonediazido group represented by formula IV or V as a photosensitive agent is exposed and developed to form a resist pattern of a prescribed shape. In the formulae II, III, (i) is 1 or 2, each of (k), (m) and (p) is an integer of 0 to 3, (n) is an integer of 1 to 4, (q) is an integer of 1 to 3, (r) is 2 or 3,  $m+p+n \leq 6$  and  $k+q \leq 5$ .



I



II



III



IV



V

## LEGAL STATUS

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22.01.1998

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examiner's decision of rejection or application converted  
registration]

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03.09.1999

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## \* NOTICES \*

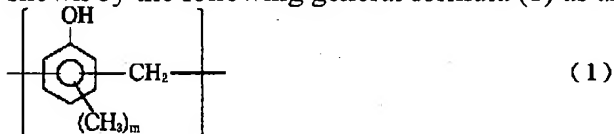
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## CLAIMS

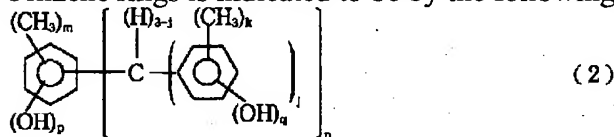
[Claim(s)]

[Claim 1] (1) The novolak resin whose polystyrene equivalent weight average molecular weight it has the repeat unit shown by the following general formula (1) as an alkali fusibility resin, and is 2000-10000 [-izing 1]



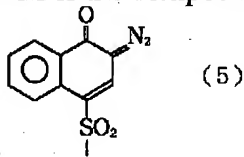
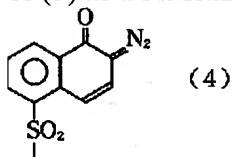
(However, the inside m of a formula is the integer of 0-3.)

(2) The low nucleophile with which have a phenolic hydroxyl group as a dissolution accelerator, and the number of the benzene rings is indicated to be by the following general formula (2) whose number is 2-5, or (3) [-izing 2]



(However, for 1 or 2, and k, m and p, 0-3n are [ 1-3r of 1-4q ] the integers of 2 or 3, respectively, and the inside j of a formula is  $m+p+n \leq 6$  and  $k+q \leq 5$ .)

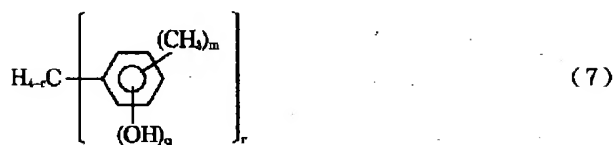
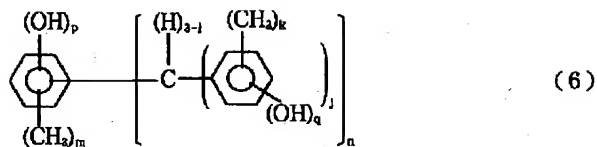
(3) It has in a molecule 1 and 2-naphthoquinonediazide sulfonyl machine shown by the following general formula (4) or (5) as a sensitization agent, and is the compound [-izing 3] of 65% or more of rates of the esterification.



The positive-resist constituent for the lift-off methods which \*\*\*\*\* and is characterized by the bird clapper.

[Claim 2] (3) The constituent according to claim 1 which used what is obtained by introducing 1,2-quinone diazide sulfonylchloride into the ballast molecule, trihydroxy benzophenone, or tetrapod hydroxy benzophenone shown by the following general formula (6) or (7) as a sensitization agent of a component.

[Formula 4]



(However, for 1 or 2, and k, m and p, 0-3n are [ 1-3r of 1-4q ] the integers of 2 or 3, respectively, and the inside j of a formula is  $m+p+n \leq 6$  and  $k+q \leq 5$ .)

[Claim 3] (1) The constituent according to claim 1 or 2 whose loadings of 10 - 60 weight section and (3) components the loadings of 80 weight sections and (2) components are 15 - 60 weight section for the loadings of a component.

[Claim 4] The pattern formation method characterized by forming a micro groove in the resist layer which constitutes the above-mentioned resist pattern in the pattern formation method by the lift-off method which consists of forming a metal layer in the base front face containing a resist pattern, exfoliating a resist pattern subsequently and forming a predetermined metal pattern on the above-mentioned base after forming a resist pattern on a base.

[Claim 5] the case where set line width of face of a resist layer to  $L_{\text{mum}}$ , and set thickness to  $T_{\text{mum}}$ , and the lobation height of a micro groove was set to  $A_{\text{mum}}$ , and the lobation depth is set to  $B_{\text{mum}}$  in the resist layer profile shown in drawing 1 or drawing 2 -- resist layer thickness  $T$  -- the grade of the lobation of 20 micrometers or less and the above-mentioned micro groove -- the following formula [I] and [II]

[Equation 1]

$$\frac{1}{20} \leq \frac{A}{T} \leq \frac{2}{5} \quad \dots [I]$$

$$\frac{1}{10} \leq \frac{A}{B} \leq 2 \quad \dots [II]$$

The pattern formation method according to claim 4 formed in \*\*\*\*\*.

[Claim 6] The pattern formation method according to claim 4 or 5 which formed the resist pattern with the positive-resist constituent according to claim 1, 2, or 3.

[Claim 7] It is the pattern formation method according to claim 6 which exposed the exposure front stirrup after performing BEKU by the 100-130-degree C temperature requirement before development, developed negatives by forming a resist film on a base with a positive-resist constituent according to claim 1, 2, or 3, and formed the micro groove in the resist layer.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] In case this invention can form the process tolerance by the lift-off method, and a reliable circuit pattern and forms circuit patterns, such as an aluminum electrode, on a semiconductor, it relates to the positive-resist constituent for the lift-off methods and the pattern formation method of using suitably.

[0002]

[Description of the Prior Art] When forming circuit patterns, such as an aluminum electrode, on a semiconductor conventionally, processes, such as dry etching and wet etching, were used. It is as being shown in drawing 3, a concrete process performs metal layer sputtering and resist patterning, after making the resist pattern 3 form on the metal layer 2 formed on the base 1, it carries out etching processing of the metal layer 2 of resist pattern 3 a non-formed portion, subsequently processes it with ablation liquid, exfoliates the resist pattern 3, and forms a circuit pattern.

[0003] However, the above-mentioned process has a problem in the etching operation in the case of using the gold of difficulty etching nature, a tantalum, etc. as the point and metal layer of a process tolerance (a VSLI manufacturing technology, Nikkei Business Publications, 1989, p259 reference), and, for this reason, the lift-off method shown in drawing 4 is used in many cases in recent years. After making the resist pattern 3 form on a base 1 by resist patterning first, this lift-off method makes the metal layer 2 form on a base 1 and the resist pattern 3 by metal layer sputtering, and it can process this with ablation liquid, and resist ablation can be carried out, and it can form a circuit pattern without etching operation. Thus, if the metal of difficulty etching nature can also be deposited on a base and a resist layer while it can perform accurate processing, since the lift-off method uses as mold the resist pattern formed with a sufficient precision and forms a metal pattern, since there is no need for etching, it has the advantage of being easily processible. The resist ablation process has played the important role especially by this lift-off method, and if a resist can be efficiently exfoliated at this process so that there may be no resist \*\*, the improvement in a process tolerance and improvement in reliability are expectable by using the lift-off method.

[0004] However, if it was going to form a pattern by the describing [ above ] lift-off method using a common positive-resist constituent, since a resist ablation process would not advance well and resist \*\* would occur, the present condition was that there is a problem in the reliability of the lift-off method etc.

[0005] That is, the biggest problem in this case is as being shown in drawing 5, and is that possibility that the resist pattern 3 serves as an order taper as shown in drawing 51, therefore the sputtering particle of the metal which comes flying with a certain amount of anisotropy adheres also to the side attachment wall of the resist pattern 3 (refer to drawing 52), and it becomes impossible for ablation liquid to attack the direct resist pattern 3 in the resist ablation process of degree process for this reason comes out in a positive resist. Moreover, the metal layer 2 adhering to the side attachment wall was thin, even when a part was destroyed and ablation liquid permeated the resist pattern 3, as shown in drawing 53, the metal pattern 4 may have become a back taper configuration, the barricade 5 may have come out, and resist \*\* 6 may have occurred further.

[0006] on the other hand, the phenomenon called micro groove is well known for the field of a positive-type photoresist from before (2 the 39th applied-physics relation union lecture meeting, collection No[ of lecture drafts ]. p 15 or 517 and 29 p-NA-1992, spring) As a reference mark 7 shows this micro groove in drawing 1 and 2, it is the deformation produced in the resist pattern bottom section, and the resist pattern 3 is the phenomenon which shows the configuration where it is hard and a it top protrudes the inside in an interface with a base 1. This phenomenon is set in the bottom section of the pattern which must be the unexposed section, since a sensitization agent collapses or disappears and the dissolution takes place, it is produced, and the sensitization agent concentration distribution is considered to be the cause.

[0007] Even if what such a phenomenon produced was excellent in resolution etc., it was a big theme in a resist development field whether generating of a micro groove is kept to the minimum by controlling the solubility of the resist which it was not used as a resist, therefore the micro groove produced how.

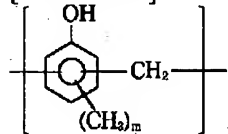
[0008] It was made in order that this invention might solve the trouble in the above lift-off methods especially, and it aims at offering the circuit pattern formation method by the lift-off method using the positive-resist constituent for the lift-off methods and this which can form a process tolerance and a reliable circuit pattern.

[0009]

[Means for Solving the Problem and its Function] In order that this invention person may attain the above-mentioned purpose, as a result of repeating examination wholeheartedly, it has the repeat unit shown by the following general formula (1) as a (1) alkali fusibility resin. The novolak resin whose polystyrene equivalent weight average molecular weight is 2000-10000, (2) The low nuclide with which have a phenolic hydroxyl group as a dissolution accelerator, and the number of the benzene rings is indicated to be by the following general formula (2) whose number is 2-5, or (3), (3) It has in a molecule 1 and 2-naphthoquinonediazide sulfonyl machine shown by the following general formula (4) or (5) as a sensitization agent. After forming a resist film especially on a base using the positive-resist constituent which comes to blend the compound of 65% or more of rates of the esterification, an exposure front stirrup carries out and develops [ expose and ] BEKU by the 100-130-degree C temperature requirement before development. The effective thing was found out in the pattern formation method according [ making the resist pattern which has the micro groove of a predetermined configuration in a resist layer form ] to the lift-off method.

[0010]

[Formula 5]

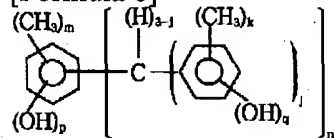


(1)

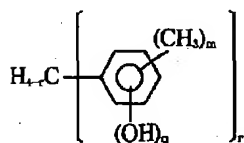
(However, the inside m of a formula is the integer of 0-3.)

[0011]

[Formula 6]



(2)

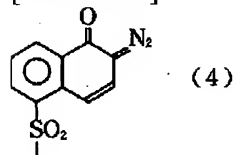


(3)

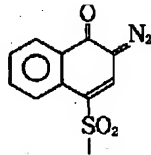
(However, for 1 or 2, and k, m and p, 0-3n are [ 1-3r of 1-4q ] the integers of 2 or 3, respectively, and the inside j of a formula is m+p+n<=6 and k+q<=5.)

[0012]

[Formula 7]



(4)



(5)

[0013] That is, in this invention, a resist layer tends to be made to discover conversely the micro groove disliked conventionally positively, and it is going to apply to the lift-off process which had become a problem with the conventional positive-resist constituent especially. The process is as being shown in drawing 6, the resist pattern 3 which uses the positive-resist constituent of this invention on a base 1, and has the micro groove 7 can be formed, metal sputtering, metal vacuum evaporation, etc. can be performed to this, the metal layer 2 can be formed, and many advantages which are described below can be produced by performing resist ablation.

(1) There are not adhesion and deposition of the metal to the micro groove portion generated to the resist pattern

bottom, ablation liquid can attack a direct resist pattern and homogeneity is promptly improved by resist ablation within fixed time.

(2) The micro groove portion generated to the resist pattern bottom exists as an opening, and after metal deposition does not have generating of resist \*\* in a corner portion in the case of resist ablation.

(3) Let the metal pattern finally obtained be the good pattern of rectangle nature.

[0014] Therefore, a process tolerance and a reliable circuit pattern can be made to form in the lift-off method according to this invention, without the conventional trouble mentioned above arising.

[0015] Therefore, this invention has the repeat unit shown by the above-mentioned general formula (1) as a [A] (1) alkali fusibility resin. The novolak resin whose polystyrene equivalent weight average molecular weight is 2000-10000, (2) The low nuclide with which have a phenolic hydroxyl group as a dissolution accelerator, and the number of the benzene rings is indicated to be by the above-mentioned general formula (2) whose number is 2-5, or (3), (3) It has in a molecule 1 and 2-naphthoquinonediazide sulfonyl machine shown by the above-mentioned general formula (4) or (5) as a sensitization agent. The positive-resist constituent for the lift-off methods which comes to blend the compound of 65% or more of rates of the esterification, [B] After forming a resist pattern on a base, form a metal layer in the base front face containing a resist pattern, and, subsequently a resist pattern is exfoliated. In the pattern formation method by the lift-off method which consists of forming a predetermined metal pattern on the above-mentioned base The pattern formation method characterized by forming a micro groove in the resist layer which constitutes the above-mentioned resist pattern [C] In the resist layer profile shown in drawing 1 or drawing 2 Line width of face of a resist layer is set to  $L_{\text{mum}}$ , and thickness is set to  $T_{\text{mum}}$ . the lobation height of a micro groove  $A_{\text{mum}}$ , When the lobation depth is set to  $B_{\text{mum}}$ , resist layer thickness  $T$  20 micrometers or less, The above-mentioned pattern formation method which formed the grade of the lobation of the above-mentioned micro groove in the following formula [I] and the range of [II], [D] The above-mentioned pattern formation method which formed the resist pattern with the above-mentioned positive-resist constituent, And [E] A resist film is formed with the above-mentioned positive-resist constituent on a base, and after an exposure front stirrup performs BEKU by the 100-130-degree C temperature requirement before development, it is exposed and develops negatives, and the above-mentioned pattern formation method which formed the micro groove in the resist layer is offered.

[0016]

[Equation 2]

$$\frac{1}{20} \leq \frac{A}{T} \leq \frac{2}{5} \quad \dots [I]$$

$$\frac{1}{10} \leq \frac{A}{B} \leq 2 \quad \dots [II]$$

[0017] Hereafter, it has per this invention and also the repeat unit the positive-resist constituent for the lift-off methods of this invention is indicated to be by the following general formula (1) as an alkali fusibility resin when it explains in detail, and the novolak resin whose polystyrene equivalent weight average molecular weight is 2000-10000 is used.

[0018]

[Formula 8]



(However, the inside m of a formula is the integer of 0-3.)

[0019] The novolak resin of the above-mentioned formula (1) is compoundable the phenols shown by the following general formula (8), and by making at least one sort and aldehydes, such as o-cresol, m-cresol, and p-cresol, specifically condense by the usual method.

[0020]

[Formula 9]



(However, the inside m of a formula is the integer of 0-3.)

[0021] In this case, as aldehydes, although formaldehyde, a paraformaldehyde, an acetaldehyde, a benzaldehyde, etc.

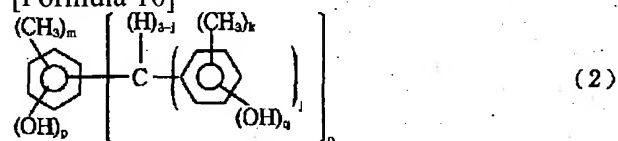
are mentioned, for example, formaldehyde is suitable. In addition, the operating rate of the phenols of the above-mentioned formula (8) and aldehydes has the desirable rate of 0.3-2 at a mole ratio.

[0022] the average molecular weight of the above-mentioned alkali fusibility resin was mentioned above -- as -- polystyrene equivalent weight average molecular weight -- 2000-10000 -- it is the range of 3000-7000 preferably. If polystyrene equivalent weight average molecular weight is smaller than 2000, the thermal resistance of a resist film will not reach practical use level, but if 10000 is exceeded conversely, the resolution of a resist film will decline.

[0023] Next, the low nuclide which has a phenolic hydroxyl group and is shown as a dissolution accelerator by the following general formula (2) whose number of the benzene rings is 2-5, or (3) is blended.

[0024]

[Formula 10]



(However, for 1 or 2, and k, m and p, 0-3n are [ 1-3r of 1-4q ] the integers of 2 or 3, respectively, and the inside j of a formula is m+p+n≤6 and k+q≤5.)

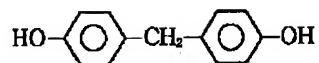
[0025] The number of the benzene rings of the above-mentioned low nuclide is 2-5, if 2 is not fulfilled, the thermal resistance of a resist film will be degraded extremely, and if 5 is exceeded, the manifestation of a micro groove will become difficult. Specifically, the following are mentioned as such a low nuclide.

[0026]

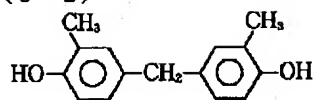
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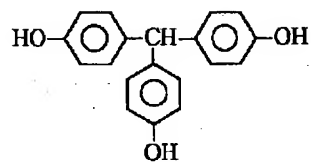
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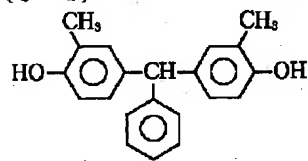
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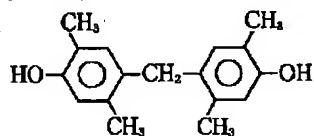
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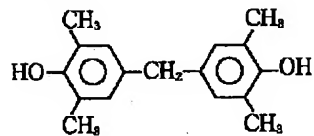
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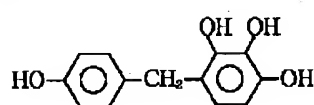
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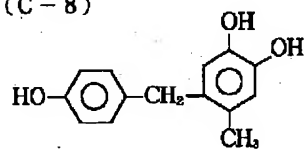
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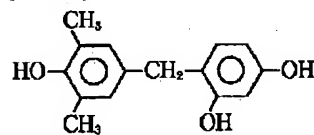
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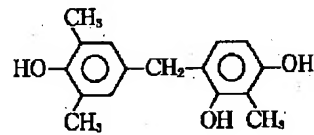
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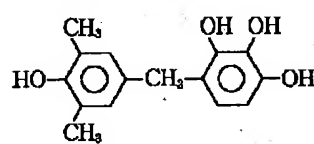
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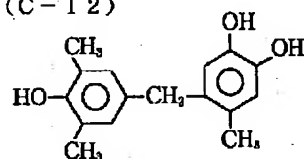
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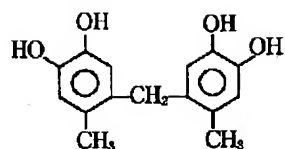
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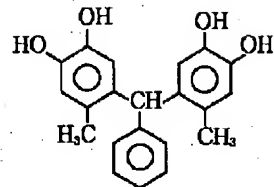
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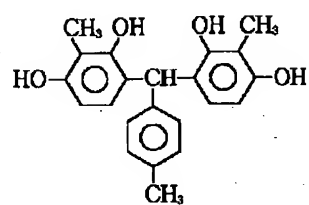
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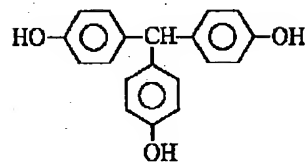
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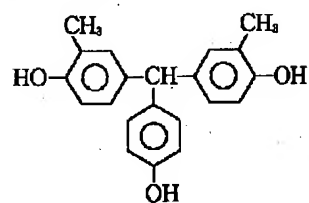
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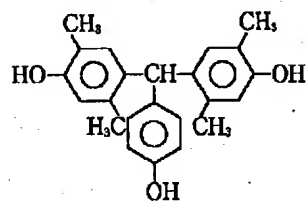
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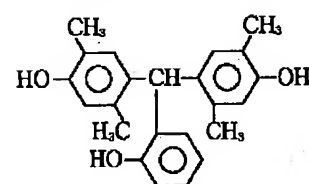
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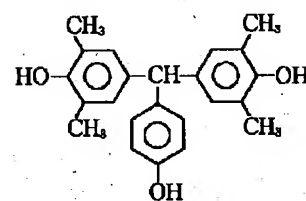
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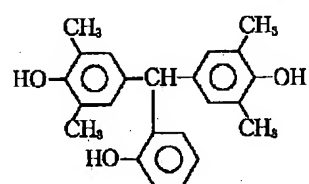
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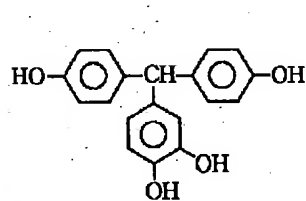
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(C-21)



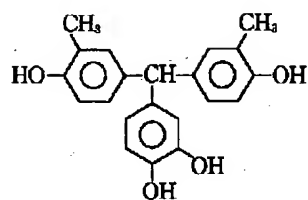
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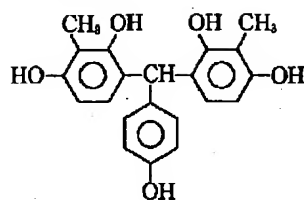
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[Formula 13]

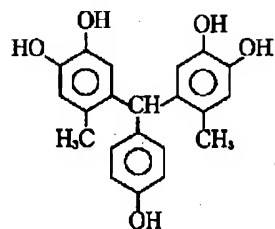
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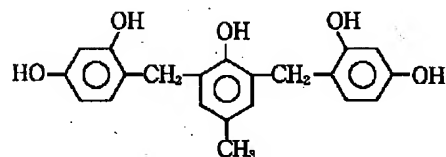
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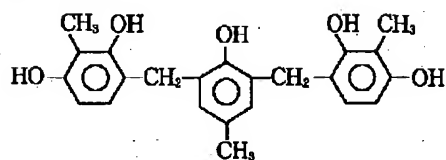
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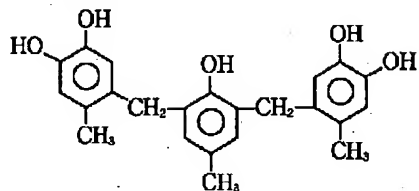
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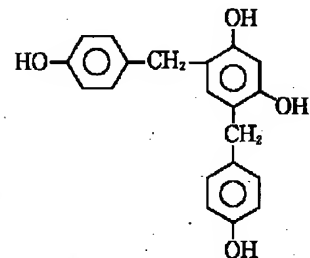
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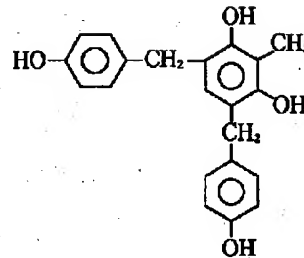
(C - 2 8)



(C - 2 9)



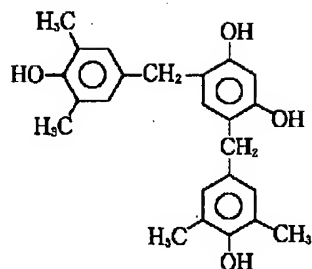
(C - 3 0)



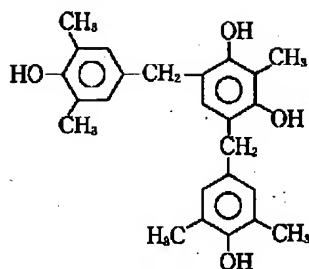
[0029]

[Formula 14]

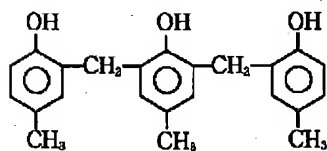
(C-31)



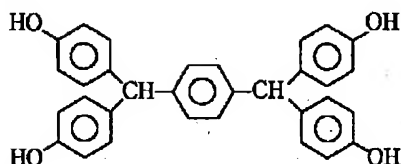
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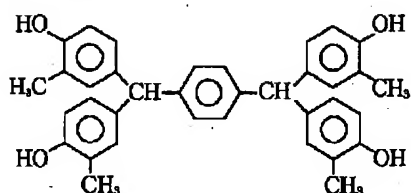
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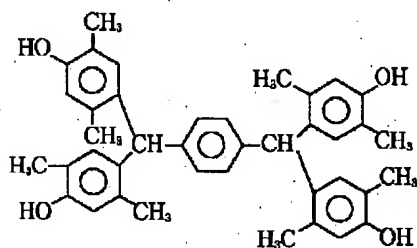
(C-34)



(C-35)



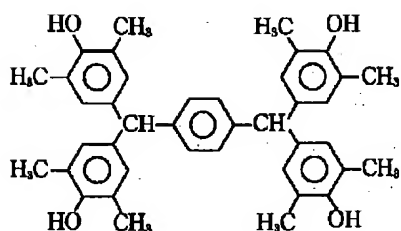
(C-36)



[0030]

[Formula 15]

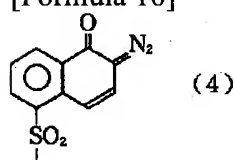
(C-37)



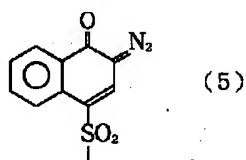
[0031] In this invention, the compound of 65% or more of rates of the esterification which have in a molecule 1 and 2-naphthoquinonediazide sulfonyl machine shown by the following general formula (4) or (5) as a sensitization agent is blended.

[0032]

[Formula 16]



(4)

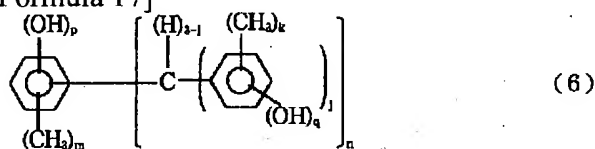


(5)

[0033] What is obtained by introducing 1,2-quinone diazide sulfonylchloride into the ballast molecule, trihydroxy benzophenone, or tetrapod hydroxy benzophenone shown by the following general formula (6) or (7) as a compound which has the above 1 and 2-naphthoquinonediazide machine, for example can use it suitably.

[0034]

[Formula 17]



(However, for 1 or 2, and k, m and p, 0-3n are [ 1-3r of 1-4q ] the integers of 2 or 3, respectively, and the inside j of a formula is  $m+p+n \leq 6$  and  $k+q \leq 5$ .)

[0035] In this case, it is desirable to use the desalting acid condensation reaction by the base catalyst of 1 and 2-NATOFU quinone diazide sulfonylchloride and a phenol nature OH basis as an introductory method, and what replaced 65% or more of the phenol nature OH basis of the ballast molecule of a formula (6) and (7), TORI, or a tetrapod hydroxy benzophenone is used suitably.

[0036] If the rate of the esterification of the compound which has the above 1 and 2-naphthoquinonediazide sulfonyl machine is 66 - 100% preferably 65% or more as mentioned above and is not filled to 65%, the manifestation of a micro groove will become difficult.

[0037] the positive-resist constituent of this invention -- the alkali fusibility resin 80 above-mentioned section (the weight section --) the following -- being the same -- the number of the benzene rings which have the phenolic hydroxyl group which receives and is shown by the above-mentioned formula (2) or (3) the low nuclide of 2-5 the ten to 60 section It is desirable to carry out 25-40 section combination of the compound of 65% or more of rates of the esterification which have 1 and 2-naphthoquinonediazide sulfonyl machine especially shown by the 20 to 40 section, the above-mentioned formula (4), or (5) especially the 15 to 60 section. If the loadings of a low nuclide do not fulfill the ten sections, the manifestation of a micro groove may become difficult, and if it exceeds the 60 sections, a pattern may melt and flow. Moreover, if the loadings of the compound which has 1 and 2-naphthoquinonediazide sulfonyl machine do not fulfill the 15 sections, the manifestation of a micro groove may become difficult, if it exceeds the 60 sections, sensitivity may fall, and generating of scum may become remarkable.

[0038] The pattern formation method by the lift-off method of this invention A resist film is formed and exposed on a base using a proper resist constituent. After developing negatives and forming the resist pattern of business, by proper methods, such as vacuum evaporation and sputtering, on the above-mentioned base front face (resist pattern non-formed portions of a resist pattern top and a base) Gold, In the lift-off method which forms metal layers, such as a tantalum, subsequently exfoliates the above-mentioned resist pattern with proper ablation liquid, and forms a predetermined metal pattern on a base As mentioned above on the resist pattern which has this micro groove, after forming a micro groove in the resist layer which constitutes the above-mentioned resist pattern and forming a metal layer, the resist pattern which has a micro groove is exfoliated.

[0039] In this case, although a micro groove may be formed in configurations, such as the shape of the shape of a square slot, and a triangular groove, as shown in drawing 1 and 2 In the resist layer profile which shows the size to drawing 1 or drawing 2 Line width of face of the resist layer 3 is set to  $L_{\text{mum}}$ , and thickness is set to  $T_{\text{mum}}$ . the lobation height of the micro groove 7  $A_{\text{mum}}$ , When the lobation depth is set to  $B_{\text{mum}}$ , it is desirable in thickness T of the resist layer 3 the following formula [I] and [II], and to form more preferably the grade of the lobation of 20 micrometers or less and the above-mentioned micro groove 7 in the range of [I'] and [II'].

[0040]

[Equation 3]

$$\frac{1}{20} \leq \frac{A}{T} \leq \frac{2}{5} \quad \dots [I]$$

$$\frac{1}{10} \leq \frac{A}{B} \leq 2 \quad \dots [II]$$

$$\frac{1}{10} \leq \frac{A}{T} \leq \frac{1}{5} \quad \dots [I']$$

$$\frac{1}{5} \leq \frac{A}{B} \leq 1 \quad \dots [II']$$

[0041] If A/T is smaller than 1/20, the case where there is little lobation and the effect in the ablation process of the lift-off method fades will arise, and if larger than two fifths, the case where a pattern breaks from a root or becomes easy to flow will arise. When A/B is smaller than 1/10, adhesion with a base is bad, on the other hand, a pattern becomes easy to flow out, if larger than 2, it is incised, and metal becomes easy to adhere also to a portion, and the resist ablation after a metal adhesion process may become difficult.

[0042] Here, although which thing may be used as the above-mentioned resist constituent as long as it can form the micro groove like the above, it is optimal to use the positive-resist constituent for lift offs concerning this invention especially mentioned above, and the above-mentioned micro groove can be effectively formed by using this resist constituent. That is, in the former, although the above-mentioned positive-resist constituent is evaded as what generates a micro groove, by this invention, this resist constituent is used effectively conversely.

[0043] When using the positive-resist constituent of this invention, after forming especially a resist film, an exposure front stirrup has effective BEKU [ the temperature of 100-130 degrees C ] before development, and, thereby, can generate a micro groove more effectively. In addition, above-mentioned BEKU of a resist film can be performed in the stage of either a prebaking process or a post exposure BEKU process. Here, unless the above-mentioned baking temperature fulfills 100 degrees C, a micro groove is not generated, but if it exceeds 130 degrees C, the case where resist ablation becomes difficult will arise. More suitable baking temperature is 100-120 degrees C.

[0044]

[Effect of the Invention] According to this invention, a process tolerance and a reliable circuit pattern can be formed by the lift-off method.

[0045]

[Example] Although a synthetic example, an example, and the example of comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example. In addition, each section is the weight section below.

[0046] Moreover, in each example, evaluation of many performances of a resist was performed by the following method.

(1) It measured by the GPC method by making mono dispersion polystyrene into a standard using the GPC column (G2000H62 G3000H63 \*\* [ G4000H61 ]) by the average weight molecular weight Mw Oriental soda company of an alkali fusibility resin on analysis conditions with a flow rate tetrahydrofuran [ a part for /and the elution solvent tetrahydrofuran of 1.5ml ], and a column temperature of 40 degrees C.

(2) The alkali solubility alkali fusibility resin of an alkali fusibility resin was made into 35% of solid contents, it was made to dissolve in an ECA solvent, and applied to the 6"Si wafer by 2000 times, the prebake was carried out on 90 degree-Cx 90-minute hot plate, and the resin film of about 3-micrometer thickness was obtained. This was applied to the development process monitor (PMS-601) by the great Japan screen company, negatives were developed by tetramethylammonium hydroxide (TMAH) 2.38%, time until a residual membrane serves as zero was measured, initial thickness was broken in time used as these residual membrane zero, and alkali solubility was displayed in on-GUROTO loam / second (A/sec).

(3) the time of defining the molecular weight (value which divided the molecular weight of a compound by the number of OH basis in 1 molecule) per [ which is expressed with the rate of esterification above-mentioned general formula (6), or (7) ] phenol nature OH basis of a compound as OH \*\*, considering the molecular weight of imagination of this OH \*\* per OH basis, and considering the rate of 1 and 2-kino diazide sulfonyl machine introduced here with the number of mols of \*\*\*\*\* -- comparatively -- having carried out .

(4) After applying the resist constituent prepared on Si wafer which carried out the adhesion promoter coat using the spin coater (SKW-636-BV) by the resist thickness great Japan screen company and carrying out a prebake on a hot plate for 90 degree-Cx 90 minutes, resist thickness was measured by the nano spec. M210 (tradename : optical thickness-measurement equipment).

(5) the optimal light exposure Eop -- spin-dry was performed after having performed paddle development for [ 23

degree-Cx ] 65 seconds, using 2.38% solution of tetramethylammonium hydroxide (TMAH) as a developer after changing the exposure time and exposing by i line (365nm) aligner X/SR[ by NIKON CORP. ]-1755i7A (numerical-aperture NA=0.50 of a lens), and carrying out a pure water rinse Subsequently, exposure energy when forming 10-micrometer line and the space pattern in the width of face of the ratio of 1:1 was defined as the optimal light exposure Eop (sensitivity) with the electron microscope (S-4100) by Hitachi, Ltd., and was searched for with it.

[0047] [Synthetic example 1] 0.30g (2.4xten - three mols) of oxalic acid 2 hydrates was taught to 3 mouth flask equipped with the synthetic agitator of an alkali fusibility resin, the capacitor, and the thermometer as 64.9g (0.60 mols), and m-cresol 43.3g (0.40 mols), 44.6g (0.55 mols) of 37-% of the weight formaldehyde solution, and a polycondensation catalyst, the flask was dipped in the oil bath, inside \*\* be held at 100 degrees C, and the polycondensation be performed for

[0048] After adding 500ml MIBK (methyl isobutyl ketone) after the reaction end and stirring for 30 minutes, the water layer was separated, the product extracted by the MIBK layer was rinsed 5 times with 300ml pure water, and after separating liquids, 4mmHg(s) performed the 150-degree C reduced pressure strip in the evaporator. Consequently, 87g of novolak resins A-1 was recoverable.

[0049] Moreover, as shown in Table 1, it compounded like the novolak resin A-1 using raw material phenols and formaldehyde, and novolak-resin A-2-4 were obtained with the yield shown in Table 1.

[0050]

[Table 1]

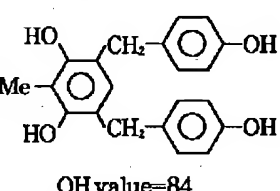
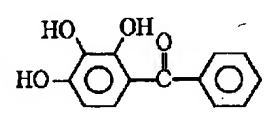
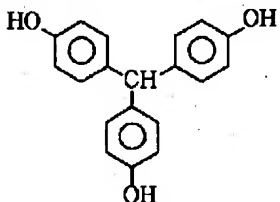
| アルカリ可<br>溶性樹脂 | 原料フェノール類 (モル) |             |                | ホルムアル<br>デヒド<br>(モル) | 収 量<br>( g ) |
|---------------|---------------|-------------|----------------|----------------------|--------------|
|               | p-クレゾ<br>ール   | m-クレ<br>ゾール | 3,5-キシ<br>レノール |                      |              |
| A - 1         | 0.60          | 0.40        | —              | 0.55                 | 87           |
| A - 2         | 0.25          | 0.55        | 0.25           | 0.60                 | 91           |
| A - 3         | 0.40          | 0.50        | 0.10           | 0.56                 | 90           |
| A - 4         | 0.50          | 0.50        | —              | 0.70                 | 92           |

[0051] [Synthetic example 2] Resorcinol derivative [ 10.0 ] (119 millimole) and 1 and 2-naphthoquinonediazide-4-sulfonyl chloride 24.0g (89.2 millimole) shown in the flask equipped with the agitator, the dropping funnel, and the thermometer under synthetic shading of 1 and 2-kino diazido compound in Table 2 was melted to 200g 1 and 4-dioxane. In order to control a flask at 25 degrees C or less, it dipped in the water bath and the catalyst which dissolved 1 and 4-diazabicyclo [ 2, 2, 2 ] octane (DABCO) 10.50g in 1 and 4-dioxane 100g was dropped using the dropping funnel. Then, the DABCO hydrochloride which deposited was filtered and removed, and it was dropped, stirring filtrate in 1800g of 0.12-N hydrochloric-acid water, and was made to reprecipitate. This was filtered further, the reprecipitation precipitate was extracted in 300ml ethyl acetate, and rinsing liquid separation was carried out 5 times with 100g pure water. The strip of this was further carried out below 40 degrees C by the evaporator, and 26g 1 and 2-quinone diazide compound B-1 was obtained.

[0052] moreover, the yield which compounds like the above 1 and 2-quinone diazide compound B-1 using resorcinol derivative [ which is shown in Table 2 ] and 1, and 2-naphthoquinonediazide sulfonyl chloride, and is shown in Table 2 -- 1 and 2-quinone diazide compound B- 2 and 3 were obtained

[0053]

[Table 2]

|     | 母核となるレゾルシン誘導体  |                      | 1,2-キノンジアジドスルホニルクロライド       |                      | 収 量   |
|-----|--|----------------------|-----------------------------|----------------------|-------|
|     | 構 造  | 重 量                  | 種 類                         | 重 量                  |       |
| B-1 | <br>OH value=84 | 10.0g<br>(119 mmol)* | 1,2-ナフトキノンジアジド-4-スルホニルクロライド | 24.0g<br>(89.2 mmol) | 26.0g |
| B-2 |                 | 10.0g<br>(130 mmol)* | 1,2-ナフトキノンジアジド-5-スルホニルクロライド | 35.0g<br>(130 mmol)  | 41.0g |
| B-3 |                 | 10.0g<br>(103 mmol)* | 1,2-ナフトキノンジアジド-5-スルホニルクロライド | 23.5g<br>(87.6 mmol) | 31.0g |

\* OH 価を分子量と仮想してモル計算した。

[0054] [Examples 1-10] After having added 1, 2-quinone diazide compound, the dissolution accelerator, and the solvent, having mixed to the alkali fusibility resin 80 section shown in Table 3, as shown in Table 3, and considering as a uniform solution, it filtered with the membrane filter of 0.2 micrometers of apertures, and the positive-resist constituent solution was prepared.

[0055] the obtained resist solution -- 6" -- it applied on the silicon wafer, the prebake for [ 90 degree-Cx ] 90 seconds was performed, and the resist film with a thickness of 3.0 micrometers was formed

[0056] Next, after irradiating radiation with a wavelength of 365nm (i line) through the recreation chill and performing PEB for [ 120 degree-Cx ] 90 seconds (post exposure baking), development, a pure water rinse, and dryness were performed. The amount of lobation of the micro groove which performed the performance evaluation of the obtained resist by the above-mentioned method, and showed the pattern profile of 10micromL/S to drawing 1 and 2 (height A, depth B) estimated. A result is shown in Table 3.

[0057] From the result of Table 3, when the pattern was formed using the positive-resist constituent of this invention, it was checked that a micro groove occurs positively and can form a process tolerance and a reliable register toss pattern.

[0058]

[Table 3]



| 実施例 | アルカリ可溶性樹脂 |      |               | 1,2-キノノンジ<br>アジド化合物 |            |            | 溶解促進剤 |            | 溶 剤   |            | 最適露<br>光量<br>E <sub>exp</sub><br>(mJ/<br>cm <sup>2</sup> ) | A<br>( $\mu$ m) | B<br>( $\mu$ m) |
|-----|-----------|------|---------------|---------------------|------------|------------|-------|------------|-------|------------|--|-----------------|-----------------|
|     | タイプ       | Mw   | アルカリ<br>溶解度   | タイプ                 | エステル<br>化率 | 添加量<br>(部) | タイプ   | 添加量<br>(部) | 種 類   | 添加量<br>(部) |  |                 |                 |
| 1   | A-1       | 2500 | 1000<br>Å/sec | B-1                 | 75 %       | 25         | C-3   | 25         | ECA   | 260        | 180  | 0.55            | 0.75            |
| 2   | A-1       | 2500 | 1000<br>Å/sec | B-2                 | 100 %      | 25         | C-8   | 25         | ECA   | 260        | 150  | 0.65            | 0.75            |
| 3   | A-1       | 2500 | 1000<br>Å/sec | B-3                 | 85 %       | 25         | C-17  | 25         | ECA   | 260        | 180  | 0.50            | 1.20            |
| 4   | A-2       | 3500 | 400<br>Å/sec  | B-1                 | 75 %       | 30         | C-25  | 22         | PGMEA | 260        | 220  | 0.40            | 0.50            |
| 5   | A-2       | 3500 | 400<br>Å/sec  | B-2                 | 100 %      | 30         | C-29  | 35         | PGMEA | 290        | 150  | 0.75            | 3.20            |
| 6   | A-3       | 3000 | 800<br>Å/sec  | B-1                 | 75 %       | 35         | C-34  | 22         | MMP   | 274        | 280  | 0.50            | 1.50            |
| 7   | A-3       | 3000 | 800<br>Å/sec  | B-2                 | 100 %      | 35         | C-34  | 30         | MMP   | 280        | 260  | 0.35            | 2.20            |
| 8   | A-3       | 3000 | 800<br>Å/sec  | B-3                 | 85 %       | 35         | C-34  | 35         | ECA   | 300        | 250  | 0.75            | 3.80            |
| 9   | A-4       | 6500 | 200<br>Å/sec  | B-1                 | 75 %       | 30         | C-3   | 25         | ECA   | 280        | 220  | 0.40            | 0.75            |
| 10  | A-4       | 6500 | 200<br>Å/sec  | B-2                 | 100 %      | 30         | C-3   | 30         | EL    | 280        | 180  | 0.50            | 1.75            |

\* ECA : エチルセロソルブアセテート  
 PGMEA : プロピレングリコールモノメチルエーテルアセテート  
 MMP : 3-メトキシメチルプロピオネート  
 EL : エチルラクトレート

[0059] [Examples 11-20] After forming Au by 5000Å \*\* on the pattern formed in the examples 1-10 using the vacuum evaporation system made from Japanese \*\* Anelva (EVD-500), it dipped for 15 minutes into the acetone solvent, and resist ablation was performed. When the pattern of Au remained and formed was observed with the electron microscope and the existence of the barricade of resist \*\* and Au was checked, it was what all do not have resist \*\* and does not generate the barricade of Au, either.

[0060] [Examples 1-4 of comparison] After having added 1, 2-quinone diazide compound, the dissolution accelerator, and the solvent, having mixed to the alkali fusibility resin 80 section, as shown in Table 4, and considering as a uniform solution, it filtered with the membrane filter of 0.2 micrometers of apertures, and the positive-resist constituent solution was prepared.

[0061] the obtained resist solution -- 6" -- it applied on the silicon wafer, the prebake for [ 90 degree-Cx ] 90 seconds was performed, and the resist film with a thickness of 3.0 micrometers was formed

[0062] Next, after irradiating radiation with a wavelength of 365nm (i line) through the recreation chill and performing PEB for [ 120 degree-Cx ] 90 seconds, development, a pure water rinse, and dryness were performed. When the performance evaluation of the obtained resist was performed by the above-mentioned method and the pattern profile of 10micromL/S was evaluated, the lobation of drawing 1 and the micro groove shown in 2 discovered neither at all.

[0063] Next, after using vacuum-evaporation-system EVD-500 and forming Au by 5000Å \*\* on the obtained pattern, it dipped for 15 minutes into the acetone solvent, and resist ablation was performed. Although the result was shown in Table 4, resist ablation of neither was completed, or even if resist ablation was completed, resist \*\* remained, and the result was poor.

[0064]

[Table 4]

| 比較例 | アルカリ可溶性樹脂 |      |              | 1,2-キノンジ<br>アジド化合物 |            |            | 溶解促進剤 |            | 溶 剤   |            | 最適露<br>光量<br>E <sub>op</sub><br>(mJ/cm <sup>2</sup> ) | A<br>(μm) | B<br>(μm) | レジスト剥離 | レジスト残 | Auパターンのバリ |
|-----|-----------|------|--------------|--------------------|------------|------------|-------|------------|-------|------------|---|-----------|-----------|--------|-------|-----------|
|     | タイプ       | Mw   | アルカリ<br>溶解度  | タイプ                | エステル<br>化率 | 添加量<br>(部) | タイプ   | 添加量<br>(部) | 種 類   | 添加量<br>(部) |   |           |           |        |       |           |
| 1   | A-2       | 3500 | 400<br>A/sec | B-1                | 75%        | 29         | なし    | なし         | PGMEA | 200        | 370   | 0         | 0         | NG     | —     | —         |
| 2   | A-2       | 3500 | 400<br>A/sec | B-1                | 75%        | 29         | C-25  | 5          | PGMEA | 210        | 340   | 0         | 0         | OK     | 有     | 有         |
| 3   | A-2       | 3500 | 400<br>A/sec | B-1                | 50%        | 30         | C-25  | 22         | PGMEA | 250        | 210   | 0         | 0         | OK     | 有     | 有         |
| 4   | A-4       | 6500 | 200<br>A/sec | B-2                | 100%       | 25         | C-3   | 8          | EL    | 230        | 230   | 0         | 0         | OK     | 有     | 有         |

[Translation done.]

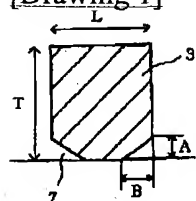
## \* NOTICES \*

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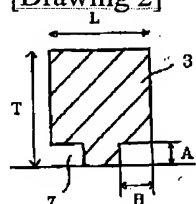
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DRAWINGS

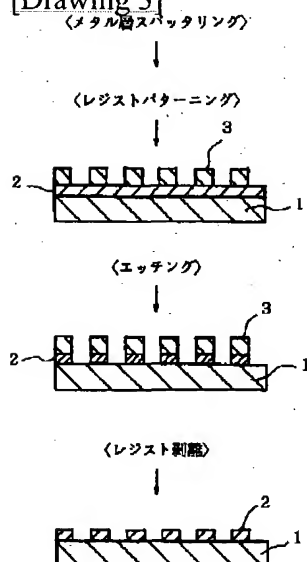
[Drawing 1]



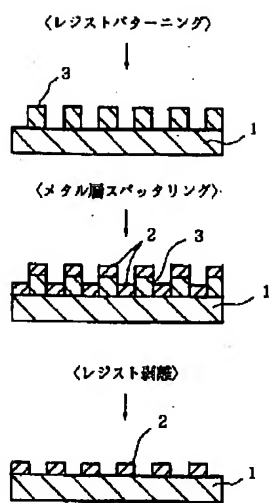
[Drawing 2]



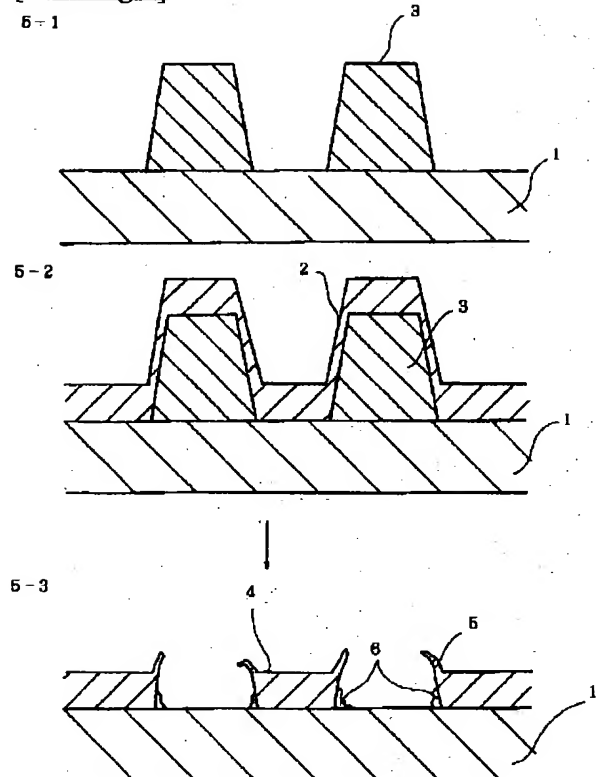
[Drawing 3]



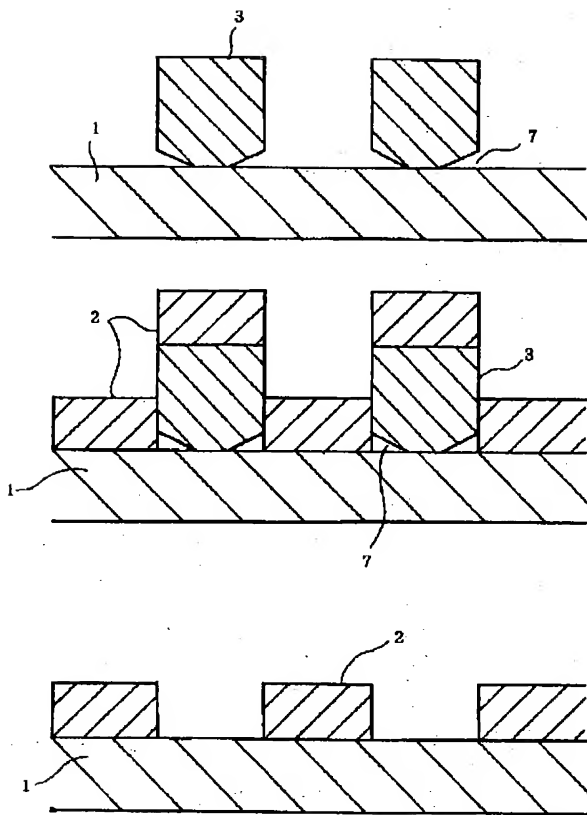
[Drawing 4]



[Drawing 5]



[Drawing 6]



[Translation done.]